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73 Proprietor : NIPPON OIL CO. LTD.
3-12, Nishi Shinbashi 1-chome
Minato-ku Tokyo (JP)
Proprietor : PETROLEUM ENERGY CENTER
2-3-22, Azabudai
Minato-ku, Tokyo (JP)

72 Inventor : Shioiri, Tomonori
1334-26 Ninomiya, Ninomiya-machi
Naka-gun, Kanagawa-ken (JP)
Inventor : Satake, Shinichi
19-8 Hisaki-cho, Isogo-ku
Yokohama-shi, Kanagawa-ken (JP)
Inventor : Sekido, Yasuo
6-28-7 Yokoudai, Isogo-ku
Yokohama-shi, Kanagawa-ken (JP)
Inventor : Fujisou, Tokuo
4-25 Miharu-cho, Yokosuka-shi
Kanagawa-ken (JP)
Inventor : Obuchi, Akira
6-1-1-5-204 Kirigaoka, Midori-ku
Yokohama-shi, Kanagawa-ken (JP)
Inventor : Kato, Hideharu
54-12 Kaminomachi, Sakae-ku
Yokohama-shi, Kanagawa-ken (JP)

74 Representative : Jander, Dieter, Dipl.-Ing. et al
Dipl.-Ing. Dieter Jander Dr.-Ing. Manfred
Böning Patentanwälte Leistikowstrasse 2
W-1000 Berlin 19 (DE)

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Description

This invention is directed to the production of hydrogen from hydrocarbons and more particularly to a process for deriving hydrogen from a hydrocarbon feed in which the starting material is subjected to stripping of its sulfur contents on a nickel sorbent and subsequently to reforming reaction on a steam reforming catalyst.

Hydrogen finds extensive application for instance as a starting material, a refining agent, a fuel and the like and has its source of supply from a variety of methods including electrolysis of water and steam reforming, partial oxidation, decomposition or dehydrogenation of hydrocarbons and alcohols. Hydrogen obtainable by electrolyzing water is highly pure, though costly, and hence applicable to special usage as in physical and chemical experiments. Hydrogen for industrial use as starting materials or product refiners is in most cases produced by steam-reforming or partially oxidizing relatively cheap, readily available materials and in such instance steam reforming of light hydrocarbons and alcohols is more often effected than partial oxidation of coals and heavy residual oils. Such light hydrocarbons and alcohols include for example methane, ethane, propane, butane and mixtures thereof and gases containing these hydrocarbons, light naphtha, heavy naphtha and methanol.

In general, hydrocarbons contain sulfur compounds which tend to adversely affect steam reforming catalysts. It is necessary therefore to remove sulfur contents from the hydrocarbon prior to reforming reaction as the catalyst is highly sensitive to those sulfur compounds.

A hydrogenative desulfurization process is known for removing sulfur compounds from hydrocarbons in the presence of a hydrogen-containing gas with the use of a catalyst such as cobalt-molybdenum, nickel-molybdenum, nickel-cobalt-molybdenum, nickel-tungsten and the like and under elevated temperature and pressure conditions. Hydrogen sulfide thus formed is subsequently removed by adsorption on to a metal oxide such as zinc oxide, copper oxide, manganese oxide or iron oxide. The resulting desulfurized mixture can be further treated in a steam reforming step. Such a process comprising catalytic hydrodesulfurization, adsorption and catalytic steam reforming is known from DE-B 1 545 446. Hydrogenative desulfurization differs in reaction conditions from steam reforming, entailing the disposition of reaction vessels, control devices, heat exchangers and other necessary facilities for use in desulfurization at a position upstream of and independently of the steam reformer. This leaves the problem that the whole apparatus gets bulky with tedious control.

With the prior method of adsorbing hydrogen sulfide with metal oxides, it has been difficult to remove sulfur compounds other than hydrogen sulfide to a

level of concentration tolerable to reforming catalysts. These metal oxides are liable to invite a sharp decline in adsorptivity on contact with steam in reforming reaction.

It has also been proposed that a nickel sorbent be used to remove traces of sulfur compounds from naphtha fractions in a naphtha reforming process for gasoline production, thereby maintaining a platinum catalyst fully activable in a subsequent reaction. In the chemical industry such sorbent has been utilized to adsorb a limited amount of sulfur contained in organic compounds as starting materials so that side reaction is alleviated during preparation of the compounds intended. The present inventors disclose certain adsorption methods in Japanese Patent Laid-Open Publication Nos. 63-35403, 1-188404, 1-188405 and 1-188406, which methods serve to remove sulfur contents from a kerosine fraction under specific conditions. However, the methods of Publication Nos. 63-35403, 1-188404 and 1-188405 have been found not still satisfactory because increased quantity of a nickel sorbent is required to achieve a 0.2 ppm level over prolonged length of time. With the method of Publication No. 1-188406, hydrogen-containing gas often outgoes together with carbon monoxide (CO) and carbon dioxide (CO₂) from a desulfurization reactor with the results that CO and CO₂ will react with H₂ in the presence of a nickel sorbent and thus generate gaseous methane, leading to hazardous heat buildup.

As hydrogen-containing gas necessary for reforming reaction, part of reformed gas derivable from that reaction is usually recycled in which CO and CO₂ are contained. This recycle gas is obtained substantially free from CO and CO₂ only when passed through carbon monoxide modifiers and carbonate removers arranged downwardly of the steam reformer. Contact of a nickel solvent with a hydrocarbon at a temperature above 40°C at an inlet of the reformer has been experimentally proved susceptible to too much carbonaceous deposit for practical purposes.

The present invention seeks to provide a novel process for producing hydrogen of high purity from hydrocarbons which will eliminate the foregoing drawbacks of the prior art methods and which will enable the hydrocarbon to react with a nickel sorbent in the presence of steam and without formation of methane. More specifically, the invention resides in the provision of a process for hydrogen production which will exhibit reduced carbonaceous deposition on and prolonged service of the nickel sorbent without involving added gas-liquid separator and heat exchanger facilities.

As will become better understood from the following description, the invention provides a process for producing hydrogen from hydrocarbons, which comprises contacting a hydrocarbon feed with a nickel-containing sorbent in the presence of steam and hy-

hydrogen-containing gas at a pressure of lower than 50.10^5 Pa (50 kg/cm²G), at a temperature of 150 to 500°C and at a GHSV of 100 to 5,000 hr⁻¹ or at an LHSV of 0.1 to 10 hr⁻¹ and subsequently treating the resulting reaction mixture with a steam reforming catalyst.

Hydrocarbons eligible for purposes of the present invention are gaseous or liquid at room temperature and at atmospheric pressure. Gaseous hydrocarbons include methane, ethane, propane, butane and the like singly or in combination and natural gas, whereas liquid hydrocarbons include light naphtha fractions, heavy naphtha fractions, kerosine fractions and the like and mixtures thereof. Particularly preferred are natural gases, light and heavy naphthas and kerosine fractions.

Naphthas usually have a content of sulfur compounds of not more than 300 ppm by weight, and kerosine fractions do a similar content of smaller than 2,000 ppm by weight. Sulfur contents in hydrocarbons suitable for the invention are not specifically restrictive but economically feasible in an amount of not more than 150 ppm by weight and preferably less than 100 ppm by weight and more preferably up to 10 ppm by weight.

Nickel sorbents according to the invention preferably contain nickel in an amount of 30 to 70% by weight and may further contain small quantities of copper, chromium, zirconium, magnesium and other metal components. Suitable carriers are selected for example from silica, alumina, silica-alumina, titania, zirconia, zinc oxide, clay, diatomaceous earth and other inorganic refractory oxides. The nickel-containing sorbent preferably takes the form of a tablet, pellet or sphere having a size of 0.5 to 10 mm. To avoid fire hazard or otherwise improve surface stability, the sorbent may be treated by partial oxidation of its nickel component or by adsorption with gaseous carbon dioxide. It may be subjected, prior to use, to hydrogen reduction at from 150 to 400°C or to carbon dioxide removal by an inert gas.

Hydrogen-containing gas may be supplied from an external source, but may more conveniently be replaced with a portion of hydrogen which is generated according to the invention and which can be recycled. A reformed gas from a steam reformer is made up of CO₂, CO, H₂O, CH₄ and traces of hydrocarbons of two or more carbon atoms normally in thermodynamic equilibrium and may be used either as generated or after removal of materials other than hydrogen. This varies depending upon the end use of hydrogen. In hydrogen-containing gas to be recycled, therefore, hydrogen may be contained in an amount of 30% or more.

A selected hydrocarbon as a starting material may be contacted with a nickel sorbent in the presence of hydrogen-containing gas and steam and under reaction conditions at a pressure of lower than

50.10^5 Pa (50 kg/cm²G) and preferably from atmospheric to 30.10^5 Pa (30 kg/cm²G) and at a temperature of 150 to 500°C and preferably from 250 to 500°C. Lower pressures of 10.10^5 Pa (10 kg/cm²G) or below are clear of the provisions of the high pressure gas ordinance and easy and simple to handle. The hydrocarbon if gaseous should be in the range of 100 to 5,000 hr⁻¹ in gas per hour space velocity (GHSV) and if liquid in the range of 0.1 to 10 hr⁻¹ and preferably from 1 to 5 hr⁻¹ in liquid per hour space velocity (LHSV). The hydrogen to hydrocarbon ratio preferably ranges from 0.05 to 1.0 Nm³ in terms of pure hydrogen/kg of hydrocarbon. Steam may be used in a steam to carbon ratio of 0.1 to 7 mol/atom and preferably 0.2 to 5 mol/atom. Smaller ratios of steam than 0.01 mol/atom would not be effective in reforming the starting hydrocarbon and greater ratios than 7 mol/atom would render the nickel sorbent less active.

The hydrocarbon and steam may be contacted with a nickel sorbent by upward or downward passage through the desulfurization reactor in which has previously been packed with that sorbent. The hydrocarbon upon treatment has a low sulfur content of 0.2 ppm by weight or below and thus suits steam reforming according to the invention.

The nickel sorbent may be packed in a vessel located in contiguous relation to, or at an inlet of, the steam reformer and should importantly be contacted with a given hydrocarbon in the presence of hydrogen-containing gas and steam. The resultant reaction mixture should thereafter be contacted as prepared with a steam reforming catalyst with or without the addition of steam.

Suitable reforming catalysts contain, as an active metal, nickel in an amount of 5 to 50% by weight as an oxide and preferably from 10 to 35% by weight and may also contain ruthenium. As carriers for this catalyst there may suitably be used those specified in connection with the nickel sorbent. A promoter may be employed which is made up such as of an oxide of an alkaline metal, an alkaline earth metal or a rare earth metal and which is added in an amount of less than 10% to prevent carbon precipitation.

Hydrocarbon reforming reaction may preferably be effected at a temperature of 400 to 600°C at a catalyst bed inlet and at from 600 to 850°C at a catalyst bed outlet, at a pressure of below 50.10^5 Pa (50 kg/cm²G) and preferably at from atmospheric to 30.10^5 Pa (30 kg/cm²G) and more preferably at lower than 10.10^5 Pa (10 kg/cm²G), at pure hydrogen-hydrocarbon ratio of 0.05 to 1.0 Nm³/kg and at a steam-carbon ratio of 2.5 to 7 mol/atom. A reformed gas is usually entrained with CO₂, CO, CH₄ and H₂O and may be further refined if necessary. CO may be removed or reduced by contacting the reformed gas with a high-temperature modifying catalyst such as Fe₂O₃-Cr₂O₃ at from 300 to 500°C and/or with a low-temperature modifying catalyst such as CuO-ZnO at

from 150 to 250°C. Where CO is required to reduce to 0.1% by volume or below, further treatment may be done by a nickel catalyst-filled methanator. CO₂ may be removed by the use of a basic material such as KOH. Hydrogen-containing gas on refining is put to use, but may in part be recycled to an inlet of the nickel sorbent bed.

Hydrogenative desulfurization and hydrogen sulfide adsorption may if necessary be carried out prior to treatment with a nickel sorbent. In this instance a selected hydrocarbon is at first contacted with a desulfurizing catalyst packed usually on top of the desulfurization reactor. Catalysts used for this reaction are composed preferably of an active metal such as of cobalt-molybdenum, nickel-molybdenum, nickel-cobalt-molybdenum or nickel-tungsten, which metal is supported on a carrier such as alumina or an alumina-based oxide. Cobalt or nickel may preferably be carried as an oxide in an amount of 2 to 7% by weight and molybdenum or tungsten as an oxide in an amount of 8 to 25% by weight. This catalyst is from 0.7 to 5 mm in diameter and 10 mm or shorter in length. It may be extruded or pelletized into a circular, trefoiled or quatre-foiled shape as seen diametrically cross-sectionally. The catalyst is reduced by hydrogen and pre-sulfurized by a sulfurizing agent either before or after it is packed in a desulfurization reactor. After this pre-treatment, the reactor is charged with a hydrocarbon and hydrogen-containing gas under specified conditions. As hydrogen-containing gas a portion of hydrogen is conveniently utilized which is produced and recycled according to the invention as noted in steam reforming.

Desulfurization conditions may be at a pressure of lower than 50.10⁵ Pa (50 kg/cm²G) and preferably 10.10⁵ Pa (10 kg/cm²G) or below, at a temperature of 250 to 400°C, at an LHSV of 0.27 to 7 hr⁻¹ and at a pure hydrogen-hydrocarbon ratio of 0.02 to 1.0 Nm³/kg.

Hydrogen sulfide derived by desulfurization should be removed with the use of an adsorbent. Adsorbents eligible for the invention are basic in nature, and they include sodium hydroxide, calcium hydroxide, monoethanolamine, isopropylamine, ZnO, CuO, Fe₂O₃-Cr₂O₃, ZnO-CuO, ZnO-MoO₃, ZnO-Fl₂O₃ and the like. Solid compounds such as ZnO are preferred for easy handling and reasonable economy particularly where sulfur contents in hydrocarbons are held below 150 ppm by weight as contemplated under the invention. The hydrogen sulfide adsorbent may be introduced together with the desulfurization catalyst into the same reactor in which the adsorbent is placed at a reactor lower outlet and the catalyst at a reactor upper inlet. Alternatively, the adsorbent may be supplied separately from the catalyst with the former agent packed in a downward reactor and with the latter catalyst fed in an upstream reactor. In the case of separate supply, the same reaction conditions should

be followed.

The following examples are provided to further illustrate the invention.

5 Example 1

A stainless tube of 20 mm in inside diameter was packed with 100 ml of a nickel-diatomaceous earth sorbent of 59% by weight of Ni, followed by pretreatment with nitrogen gas at 200°C and by subsequent heating at 430°C. Into the tube was incorporated a naphtha feed of 34 to 170°C in boiling point, 0.656 g/cc in density and 43 ppm by weight of sulfur together with steam and hydrogen-containing gas of 74% in H₂, 24% in CO₂, 1% in Co and 1% in CH₄ each by volume. The pressure was at 2.10⁵ Pa (2 kg/cm²G), the hydrogen-naphtha ratio at 0.15 l/g, the steam-carbon ratio at 3.5 mol/atom and the LHSV at 0.35 hr⁻¹ (35 ml/hr). The temperature rised to 450°C at a sorbent bed outlet, meaning that the naphtha feed fully decomposed into a gas stream and a steam stream. The gas stream, composed of 40.1% in H₂, 20.5% in CO₂, 0.6% in CO and 38.9% in CH₄ each by volume, was reduced in its sulfur content to below 0.1 ppm by volume. It was taken as prepared into a stainless reformer of 20 mm in inside diameter in which were placed at upper and lower positions two commercial grades of reforming catalysts in their respective amounts of 17.5 ml. One grade contained 21% by weight of NiO and the other 10% by weight of NiO. Heating at 450°C at a catalyst bed inlet and at 800°C at a catalyst bed outlet gave a hydrogen-containing gas having 71.8% of H₂, 14.2% of CO₂, 12.8% of CO and 1.2% of CH₄ each by volume on a dry basis. This gas after being cooled to 200°C was supplied, at a GHSV of 1,000 hr⁻¹ on a dry basis, on to a commercial grade of a low-temperature modifying catalyst after which there was obtained hydrogen of 74% in H₂, 24% in CO₂, 1.0% in CO and 1.0% in CH₄ each by volume.

After a lapse of 600 hours following the initiation of naphtha feed, the sulfur content in the gas resulting from the sorbent bed outlet exceeded 0.1 ppm by volume. At that time feeding was brought to an end. This is interpreted to indicate that commercially available naphtha of 0.5 ppm by weight of sulfur, as against the 43 ppm naphtha now used for accelerated test, can be run even for 50,000 hours or longer under the same reaction conditions.

50 Example 2

A stainless tube of 20 mm in inside diameter was filled with 40 ml of a nickel-silica sorbent of 38% by weight of Ni. Reduction was done with hydrogen at 200°C and then heating at 400°C. The tube was charged with a commercial grade of JIS No. 1 kerosine together with steam and hydrogen-containing gas of the same composition as was in Example 1.

Reaction conditions were at a pressure of 9.10^6 Pa (9 kg/cm²G), at a hydrogen-kerosine ratio of 0.5 l/g, at a steam-carbon ratio of 4.5 mol/atom and at an LHSV of 1 hr⁻¹ (40 ml/hr). The tube showed a temperature of 430°C at its sorbent bed outlet so that treated kerosine had a sulfur content below 0.1 ppm by volume. Into a stainless reformer of 20 mm in inside diameter was incorporated the resulting gas stream, followed by contact with 60 ml of a reforming catalyst packed in that reformer and composed of 35% by weight of NiO. On heating at 430°C at an inlet and at 780°C at an outlet there was obtained hydrogen with 69.7% of H₂, 16.5% of CO₂, 12.5% of CO and 1.3% of CH₄ each by volume.

Kerosine feeding was discontinued after a lapse of 230 hours for reasons noted in Example 1. A long run of about 17,000 hours has been found effectively possible with a kerosine feed of 0.5 ppm by weight of sulfur.

Example 3

A stainless tube of 20 mm in inside diameter was filled with 25 ml of a nickel-diatomaceous earth sorbent of 63.7% by weight of Ni. Nitrogen treatment was effected at 200°C, and the temperature was elevated to 450°C. Natural gas was thereafter brought into contact with the sorbent also with the addition of steam and hydrogen-containing gas. The natural gas used was composed of 90% of methane, 4% of ethane, 4% of propane, 2% of butane and 4 ppm of sulfur each by volume and the hydrogen-containing gas of the same nature as in Example 1. Contact conditions were at a pressure of 1.10^5 Pa (1 kg/cm²G), at a hydrogen-natural gas ratio of 0.7 1/1, at a steam-carbon ratio of 3.0 mol/atom and at a GHSV of 2,000 hr⁻¹ (50 l/hr). Treated natural gas was reduced in its sulfur content to below 0.1 ppm by volume at 470°C at a sorbent bed outlet. This gas stream was contacted with 50 ml of a commercial reforming catalyst packed in a stainless reformer of 20 mm in inside diameter and made up of 9% by weight of NiO and also of 4% by weight of La as a promoter. Heating the catalyst bed inlet at 470°C and the catalyst bed outlet at 820°C produced hydrogen having a composition of 74.2% of H₂, 11.3% of CO₂, 14.1% of CO and 0.4% of CH₄ each by volume.

Performance was evaluated in a manner described in Example 1. Satisfactory results were obtained even over 2,400 hours. A run as long as about 9,500 hours has been proved feasible with a GHSV of 500 hr⁻¹ in place of the same velocity of 2,000 hr⁻¹.

Comparative Example 1

In a stainless tube of a 20 mm-inside diameter was supplied 40 ml of a Ni-Al₂O₃-MgO sorbent with a nickel content of 35% by weight. The sorbent after be-

ing nitrogen-treated was heated at 440°C and contacted with 40 ml of a naphtha fraction of 34 to 170°C in boiling point, 0.655 g/cc in density and 39 ppm by weight of sulfur. The pressure was at 2.10^5 Pa (2 kg/cm²G), the hydrogen-naphtha ratio at 0.15 l/g and the LHSV at hr⁻¹ (40 ml/hr). Hydrogen-containing gas used was as specified in Example 1.

This control system resulted in a failure as it showed a sharp rise in reaction temperature immediately after the test commenced. The reason was that CO or CO₂ in the hydrogen-containing gas reacted with H₂ to transform into methane. This will contribute to the reason why the inventive process requires the presence of steam. Naphtha outgoing from the system slightly smelled like hydrogen sulfide. The majority of sulfur contents was found to be discharged as hydrogen sulfide without arrest on the nickel-containing sorbent.

Example 4

A stainless desulfurization reactor of a 20 mm-inside diameter was filled at its upper portion with 40 ml of a desulfurization catalyst and at its lower portion with 40 ml of a hydrogen sulfide adsorbent. The catalyst consisted of 3.0% of NiO, 22% of MoO₃ and 75% of Al₂O₃ each by weight. ZnO was used as the adsorbent. Treatment was carried out with a mixture of a hydrogen-containing gas [74% of H₂, 24% of CO₂, 1% of CO and 1% of CH₄ each by volume], and a commercial grade kerosine [90 ppm by weight of sulfur, 50°C in flash point, 0.790 (15/4°C) in density and 153 to 260°C in boiling point]. Treated kerosine was reduced in its sulfur content to 4 ppm by weight. A mixture of treated kerosine and hydrogen-containing gas was added with steam at a temperature of 183°C and at a steam-carbon ratio of 1.4 mol/atom, followed by downward passage through the reactor packed further with 20 ml of a sorbent of 63.7% by weight of Ni. The pressure was at 9.10^6 Pa (9 kg/cm²G), the inlet temperature at 250°C and the outlet temperature at 280°C. Treated kerosine was maintained in its sulfur content at below 0.1 ppm by weight for a passage of time as long as 10,125 hours.

The resulting gaseous mixture of kerosine, hydrogen-containing gas and steam was further treated with steam at a steam-carbon ratio of 5.0 mol/atom, followed by heat exchange and by subsequent introduction into a steam reformer having packed 115 ml of a reforming catalyst of 34% by weight of NiO. Reaction conditions were at a pressure of 8.10^5 Pa (8 kg/cm²G), at an inlet temperature of 500°C and at an outlet temperature of 800°C. A gas stream was obtained which was composed of 72.0% in H₂, 14.2% in CO₂, 12.8% in CO and 1.0% in CH₄ each by volume on a dry basis. This stream was heat-exchanged to cool at 200°C and contacted at a GHSV of 1,000 hr⁻¹ with a commercial grade of a low-temperature

modifying catalyst of CuO-ZnO-Al₂O₃ after which there was produced hydrogen of 74% in H₂, 24% in CO₂, 1.0% in CO and 1.0% in CH₄ each by volume.

With the inventive process hydrogen is efficiently producible with kerosine of 90 ppm by weight of sulfur even over about 10,000 hours.

Example 5

The same grade of kerosine and conditions of desulfurization as in Example 4 were used to reduce the sulfur content to 4 ppm by weight. A mixture of treated kerosine and hydrogen-containing gas was exposed to steam at a temperature of 183°C and at a steam-carbon ratio of 0.4 mol/atom, followed by contacting with a nickel-containing sorbent in a stainless desulfurization reactor. The nickel content and the amount of the sorbent was 37.7 by weight and 40 ml, respectively. Reaction was effected at a pressure of 9.10⁵ Pa (9 kg/cm²G), at an inlet temperature of 280°C and at an outlet temperature of 320°C. The sulfur content of treated kerosine was held at below 0.1 ppm by weight for a length of time of 9,000 hours.

The above reaction mixture after being subjected to steaming at a steam-carbon ratio of 5.0 mol/atom was reacted under the same conditions as in Example 4, thereby providing hydrogen of 74% in H₂, 24% in CO₂, 17% in CO and 1% CH₄ each by volume.

The indication is that hydrogen production is highly feasible as long as about 9,000 hours.

Example 6

In a stainless desulfurization reactor of a 20 mm-inside diameter were packed 80 ml of a desulfurization catalyst and 80 ml of a hydrogen sulfide adsorbent. The catalyst and adsorbent were as used in Example 4, and the desulfurization conditions of Example 1 were followed except that the magnitude of LHSV was changed to 0.5 hr⁻¹. Contact-treated was a commercial grade of kerosine of 38 ppm by weight of sulfur, 52°C in flash point, 0.7919 (15/4°C) in density and 149 to 250°C in boiling point. Treated kerosine was reduced in its sulfur content to 0.68 ppm by weight.

The resulting gaseous mixture was further steam-treated at a temperature of 183°C and at a steam-carbon ratio of 4.5 mol/atom and subsequently heat-exchanged to contact with 40 ml of a sorbent containing 59.6% by weight of Ni. The pressure was at 9.10⁵ Pa (9 kg/cm²G), the inlet temperature at 450°C and the outlet temperature at 480°C. The sulfur content in kerosine was held at below 0.1 ppm by weight for extended time of 8,100 hours. The reaction mixture as treated was allowed to pass through a steam reformer in which two different reforming catalysts were filled in their respective amounts of 40 ml at upper and lower portions. One catalyst contained

21.0% by weight of NiO and the other 10.0% by weight of NiO. Reaction was done at a pressure of 8.10⁵ Pa (8 kg/cm²G), at an inlet temperature of 480°C and at an outlet temperature of 800°C, thereby providing hydrogen of 71.7% in H₂, 10.6% in CO, 0.4% in CH₄ and 17.3% in CO₂ each by volume on a dry basis.

As is apparent from the test results, hydrogen production is possible for about 8,000 hours.

Comparative Example 2

A stainless desulfurization reactor of a 20 mm-inside diameter was packed at its upper portion with 40 ml of a desulfurization catalyst and at its lower portion with 40 ml of a hydrogen sulfide adsorbent. The catalyst was of 3.0% in NiO, 22% in MoO₃ and 75% Al₂O₃ each by weight, and the adsorbent was ZnO. A commercial grade of kerosine was contacted at a pressure of 10.10⁵ Pa (10 kg/cm²G), at a temperature of 380°C, at an LHSV of 1.0 hr⁻¹ and at a hydrogen-kerosine ratio of 0.5 Nm³/kg. The hydrogen-containing gas was of 74% in H₂, 24% in CO₂, 1% in CO and 1% in CH₄ each by volume, and the kerosine was of 90 ppm by weight of sulfur, 50°C in flash point, 0.7903 (14/4°C) in density and 153 to 260°C in boiling point. Treated kerosine was reduced in its sulfur content to 4 ppm by weight.

The gaseous mixture was further contacted with 20 ml of a sorbent of 63.7% by weight of Ni, without the addition of steam, by downward passage through the reactor. Reaction conditions were at a pressure of 9 kg/cm²G and at an inlet temperature of 250°C. Upon initiation of the reaction, the reactor revealed hazardous temperature rise, making the test difficult to continue. This was attributed to methane formation noted in Comparative Example 1.

Claims

1. A process for producing hydrogen from hydrocarbons, which comprises contacting a hydrocarbon feed with a nickel-containing sorbent in the presence of steam in a ratio of steam to carbon of 0.1 to 7.0 mol/atom and hydrogen-containing gas at a pressure of lower than 50.10⁵ Pa (50 kg/cm²G), at a temperature of 150 to 500°C and at a GHSV of 100 to 5,000 hr⁻¹ or at an LHSV of 0.1 to 10 hr⁻¹ and subsequently treating the resulting reaction mixture with a steam reforming catalyst.
2. The process according to claim 1 wherein the hydrocarbon feed has a sulfur content of smaller than 150 ppm by weight.
3. The process according to claim 1 wherein the hydrocarbon feed is one gaseous member selected

from the group consisting of methane, ethane, propane and butane alone or in combination and natural gas.

4. The process according to claim 1 wherein the hydrocarbon feed is one liquid member selected from the group consisting of light naphtha, heavy naphtha and kerosine alone or in combination.

5. The process according to claim 1 wherein the sorbent has a nickel content of 30 to 70% by weight.

6. The process according to claim 1 wherein the catalyst contains nickel as an oxide in an amount of 5 to 50% by weight.

7. The process according to claim 1 further including hydrogenative desulfurization and hydrogen sulfide adsorption prior to contact of the hydrocarbon feed with the sorbent.

8. The process according to claim 7 wherein the hydrogenative desulfurization is accomplished by the use of a desulfurization catalyst.

9. The process according to claim 7 wherein the hydrogen sulfide adsorption is accomplished by the use of an adsorbent.

10. The process according to claim 8 wherein the desulfurization catalyst is made up of one member selected from the group consisting of cobalt-molybdenum, nickel-molybdenum, nickel-cobalt-molybdenum and nickel-tungsten.

11. The process according to claim 9 wherein the adsorbent used in the hydrogen sulfide adsorption is one member selected from the group consisting of sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide, monoethanolamine, diethanolamine, isopropylamine, zinc oxide, copper oxide, iron oxide-chromium oxide, zinc oxide-copper oxide, zinc oxide-molybdenum oxide and zinc oxide-iron oxide.

10h⁻¹ und bei dem anschließend das resultierende Reaktionsgemisch mit einem Katalysator zur Umformung des Dampfes behandelt wird.

5 2. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoff-Produkt einen Schwefelanteil kleiner als 150 Gewichts-ppm hat.

10 3. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoff-Produkt ein Gas der Gruppe: Methan, Äthan, Propan und Butan oder einer Mischung derselben und Erdgas ist.

15 4. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoff-Produkt eine Flüssigkeit der Gruppe: leichtes Naphta, schweres Naphta und Kerosin oder einer Mischung derselben ist.

20 5. Verfahren nach Anspruch 1, bei dem das Sorbent einen Nickelanteil von 30 - 70 Gew.% hat.

25 6. Verfahren nach Anspruch 1, bei dem der Katalysator Nickel als Oxid in einer Menge von 5 bis 50 Gew.% enthält.

30 7. Verfahren nach Anspruch 1, bei dem vor dem Kontakt des Kohlenwasserstoff-Produktes mit dem Sorbent eine wasserstoffaktive Entschwefelung und eine Schwefelwasserstoff-Adsorption erfolgt.

35 8. Verfahren nach Anspruch 7, bei dem die wasserstoffaktive Entschwefelung unter Verwendung eines Entschwefelungs-Katalysators durchgeführt wird.

9. Verfahren nach Anspruch 7, bei dem die Schwefelwasserstoff-Adsorption unter Verwendung eines Adsorbents durchgeführt wird.

40 10. Verfahren nach Anspruch 8, bei dem der Entschwefelungs-Katalysator aus der Gruppe: Kobalt-Molybdän, Nickel-Molybdän, Nickel-Kobalt-Molybdän und Nickel-Wolfram erstellt worden ist.

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Patentansprüche

1. Verfahren zur Erzeugung von Wasserstoff aus Kohlenwasserstoffen, bei dem ein Kohlenwasserstoff-Produkt mit einem nickelhaltigen Sorbent kontaktiert wird in Gegenwart von Dampf in einem Verhältnis von Dampf zu Kohlenstoff von 0,1 bis 7,0 Mol/Atom und von einem Wasserstoff enthaltenden Gas bei einem Druck kleiner als $50 \cdot 10^5$ Pa ($50 \text{ kg}/\text{cm}^2\text{G}$), bei einer Temperatur von 150 bis 500°C und bei einem GHSV von 100 bis 5000 h^{-1} oder einem LHSV von 0,1 bis

10h⁻¹ und bei dem anschließend das resultierende Reaktionsgemisch mit einem Katalysator zur Umformung des Dampfes behandelt wird.

2. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoff-Produkt einen Schwefelanteil kleiner als 150 Gewichts-ppm hat.
3. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoff-Produkt ein Gas der Gruppe: Methan, Äthan, Propan und Butan oder einer Mischung derselben und Erdgas ist.
4. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoff-Produkt eine Flüssigkeit der Gruppe: leichtes Naphta, schweres Naphta und Kerosin oder einer Mischung derselben ist.
5. Verfahren nach Anspruch 1, bei dem das Sorbent einen Nickelanteil von 30 - 70 Gew.% hat.
6. Verfahren nach Anspruch 1, bei dem der Katalysator Nickel als Oxid in einer Menge von 5 bis 50 Gew.% enthält.
7. Verfahren nach Anspruch 1, bei dem vor dem Kontakt des Kohlenwasserstoff-Produktes mit dem Sorbent eine wasserstoffaktive Entschwefelung und eine Schwefelwasserstoff-Adsorption erfolgt.
8. Verfahren nach Anspruch 7, bei dem die wasserstoffaktive Entschwefelung unter Verwendung eines Entschwefelungs-Katalysators durchgeführt wird.
9. Verfahren nach Anspruch 7, bei dem die Schwefelwasserstoff-Adsorption unter Verwendung eines Adsorbents durchgeführt wird.
10. Verfahren nach Anspruch 8, bei dem der Entschwefelungs-Katalysator aus der Gruppe: Kobalt-Moybdän, Nickel-Molybdän, Nickel-Kobalt-Molybdän und Nickel-Wolfram erstellt worden ist.
11. Verfahren nach Anspruch 9, bei dem das Adsorbent für die Schwefelwasserstoff-Adsorption zu der Gruppe: Natrium-Hydroxid, Kalium-Hydroxid, Magnesium-Hydroxid, Kalzium-Hydroxid, Monoäthanolamin, Diäthanolamin, Isopropylamin, Zinkoxid, Kupferoxid, Eisen-Oxid-Chrom-Oxid, Zink-Oxid-Kupfer-Oxid, Zink-Oxid-Molybdän-Oxid und Zink-Oxid-Eisen-Oxid gehört.

Revendications

1. Procédé de préparation d'hydrogène à partir

d'hydrocarbures, selon lequel on met en contact une charge de départ hydrocarbonée avec un sorbant contenant du nickel, en présence de vapeur d'eau selon un rapport de la vapeur d'eau au carbone de 0,1 à 7,0 moles/atom, et un gaz contenant de l'hydrogène sous une pression inférieure à 50.10^5 Pa (pression relative : 50 kg/cm²), à une température de 150 à 500 °C et selon une vitesse spatiale horaire du gaz de 100 à 5000 h⁻¹, ou selon une vitesse spatiale horaire du liquide de 0,1 à 10 h⁻¹, et on traite ensuite le mélange réactionnel résultant avec un catalyseur de reforage à la vapeur d'eau.

2. Procédé selon la revendication 1, dans lequel l'hydrocarbure de départ a une teneur en soufre inférieure à 150 ppm en poids. 15

3. Procédé selon la revendication 1, dans lequel l'hydrocarbure de départ est un gaz choisi parmi le méthane, l'éthane, le propane et le butane seuls ou en association, ainsi que le gaz naturel. 20

4. Procédé selon la revendication 1, dans lequel l'hydrocarbure de départ est un liquide choisi parmi le naphta léger, le naphta lourd et le kérósène, seuls ou en association. 25

5. Procédé selon la revendication 1, dans lequel le sorbant a une teneur en nickel de 30 à 70 % en poids. 30

6. Procédé selon la revendication 1, dans lequel le catalyseur contient du nickel sous la forme d'un oxyde, selon une quantité de 5 à 50 % en poids. 35

7. Procédé selon la revendication 1, comprenant en outre une désulfuration par hydrogénéation et une adsorption de sulfure d'hydrogène avant de mettre en contact l'hydrocarbure de départ avec le sorbant. 40

8. Procédé selon la revendication 7, dans lequel la désulfuration par hydrogénéation est effectuée en employant un catalyseur de désulfuration. 45

9. Procédé selon la revendication 7, dans lequel l'adsorption du sulfure d'hydrogène est effectuée en employant un adsorbant. 50

10. Procédé selon la revendication 8, dans lequel le catalyseur de désulfuration comprend un métal choisi parmi le cobalt-molybdène, le nickel-molybdène, le nickel-cobalt-molybdène, et le nickel-tungstène. 55

11. Procédé selon la revendication 9, dans lequel l'adsorbant employé dans l'adsorption du sulfure d'hydrogène, est choisi parmi l'hydroxyde de sodium, l'hydroxyde de potassium, l'hydroxyde de magnésium, l'hydroxyde de calcium, la monoéthanolamine, la diéthanolamine, l'isopropylamine, l'oxyde de zinc, l'oxyde de cuivre, l'oxyde de fer-oxyde de chrome, l'oxyde de zinc-oxyde de cuivre, l'oxyde de zinc-oxyde de molybdène et l'oxyde de zinc-oxyde de fer.